Final Report: Molecular Beam Assembly (MBA) of Graphene Nanoribbons

(GNRs): Synthesis, Transport Study, and Flexible Electronics

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INTRODUCTION:

Since the rise of graphene, it has attracted strong attention due to its exceptional electronic, ¹ thermal, ^{2,3} mechanical, ^{4,5} and optical properties. ⁶⁻⁸ Due to the lack of an energy bandgap in graphene, electronic applications of graphene have been limited to functionalities where switching off the device is not necessary. Accordingly, technologies such as graphene radio frequency transistors have been drawing lots of attention because it is easily implementable in real life applications. ⁹⁻¹¹On the contrary, digital electronics applications require a sufficient bandgap for the channel material in order to switch off the device for proper operation. As a result, extensive research was done to use graphene as a digital switch by employing novel device structures that made use of the high tunability of graphene Fermi level. ¹²⁻¹⁶Although these devices perform fairly well, their structures are complex and lack the use of excellent charge transport properties of graphene. On the other hand, numerous efforts to induce a bandgap in graphene by chemical modification, ¹⁷⁻¹⁹ use of multilayer graphene with dual gates, ²⁰⁻²² and other methods²³ were devoted. Nevertheless, these methods are either difficult to control or devices fail to perform well.

Recently, the narrowing of graphene into stripes with widths ~ 10 nm was studied both theoretically²⁴ and experimentally²⁵ to create an energy bandgap in the electronic structure of graphene due to quantum confinement. However, the theoretical predictions and the experimental data did not match due to inability to control edge structures.²⁶ Consequently, several methods were used to create

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GNRs including top down etching of graphene into GNR, ^{25, 27, 28}unzipping of carbon nanotubes, ²⁹⁻³³ chemically producing GNR, 34-36 bottom-up chemical synthesis, 37-39 and various methods for producing arrays of GNR. 33, 40-45 Additionally, several interesting transport properties were experimentally tested for several types of GNRs. 46, 47 Nevertheless, in order to create a reliable technology that uses GNR as a platform, better control of GNR should be accomplished. And issues like width control, ribbon to ribbon variations, and the quality of the materials have to be precisely and reproducibly controlled. These features are essential to control the electronic characteristics of the devices fabricated and proper operation of complex circuits. In this report, we present our efforts to study the properties of top-down GNRs and bottom-up synthesized GNRs and utilized them in applications such as chemical sensing and thin-film transistors (TFT). For top-down GNRs, we used helium ion beam lithography (HIBL) to create GNR field-effect transistors (GNR FETs) with highly dense GNR arrays with one of the smallest half-pitch GNR reported to date (5 nm). Moreover, we used chemically synthesized GNRs because the controlled widths and edge structures of bottom-up GNRs allow precise control over the electrical and optical properties of GNRs which is important for numerous applications. By studying both long chemically synthesized GNRs and short ones (i.e. nanographenes), we were able to establish new deposition techniques and unique applications for such GNRs. The results presented in this report are first steps to understanding the properties of chemically synthesized GNRs and exploring their potential applications in electronics and sensing.

PATTERNING, CHARACTERIZATION AND CHEMICAL SENSING APPLICATIONS OF GRAPHENE NANORIBBON ARRAYS DOWN TO 5 NM USING HELIUM ION BEAM LITHOGRAPHY:

In this section, we report our results in using HIBL for high resolution patterning of graphene down to 5 nm half-pitch arrays (Figure 1). We were able to control the aspect ratio of the GNRs up to 400 (i.e. the widths and lengths of GNRs are 5 nm and 2000 nm, respectively). These reduced

dimensions are enabled by the small scattering size and the small scattering lengths of helium ion beam. We performed low temperature output characteristic (i.e. I_d - V_d) measurements of a device to study the nature of thermionic activation of carriers through the graphene/GNR junction. For this device, GNRs with a width of 5 nm and length of 200 nm were patterned. Figure 2 shows the temperature dependence of the I_d - V_d curves with clear reduction of the conductance as the temperature is reduced. The nonlinearity of the differential conductance near the zero bias point (i.e. V_d = 0 V) is clearly shown for lower temperatures in Figure 2b. This effect indicates a potential barrier created for carriers transporting through graphene/GNR junction. Moreover, estimation of the activation energy (EA) was carried out using the minimum conductance value for each temperature point. Figure 2c shows that the minimum conductance (Gmin) points fit with the thermally activated carriers' equation:

$$G_{\min} = G_1 e^{\frac{-E_A}{K_B T}}$$

Where G_1 is a constant, K_B is Boltzmann's constant, T is the absolute temperature, and E_A is the activation energy. The curve fitting yielded an E_A of 44 meV and the GNR bandgap (E_G) is therefore estimated to be > 88 meV. Finally, we measured the sensitivity of GNR arrays to NO_2 gas and observed ppb level sensitivity, which shows the potential for using HIBL GNR arrays for sensing applications.

DEPOSITION, CHARACTERIZATION, AND THIN-FILM-BASED CHEMICAL SENSING OF ULTRA-LONG CHEMICALLY SYNTHESIZED GRAPHENE NANORIBBONS:

In this section we report optimized conditions for deposition and visualization of individual bottom-up chemically synthesized GNRs and films on Si/SiO₂ substrates (Figure 3), and their applications as devices and chemical sensors. We have studied different annealing conditions and their effect on GNR thin-film devices using attenuated-total-reflectance Fourier-transform infrared

spectroscopy (ATR-FTIR), electrical measurements and Raman spectroscopy which revealed the enhanced conductivity of GNR films after annealing due to the dodecyl side chains removal. AFM of individual deposited GNRs revealed GNRs with a length of >500 nm and a thickness of ~ 0.78 nm Additionally, Raman spectroscopy of individual deposited GNRs showed characteristic D, G, 2D, and D+D' peaks and electrical measurements on an individual GNR confirmed the conductivity of such GNRs. Finally, we have demonstrated an application of the GNR thin-film devices by measuring the sensitivity of such GNRs to NO₂ gas and observed ppb level sensitivity, highlighting the potential for using chemically synthesized GNRs for cost-conscious and scalable sensing applications. Our GNR film sensors exhibit high sensitivities comparing favorably to other graphene-based NO₂ sensors. We observed $\Delta G/G_0$ of ~5.6% for NO₂ concentration of 50 ppb. We attribute this enhanced NO₂ sensitivity to the semiconducting nature of chemically synthesized GNRs which allows higher level of current modulation via adsorption of NO₂ molecules than semimetal pristine graphene. Additionally, compared to graphene, edges of GNRs are more chemically active than pristine Sp² surface of graphene which might play an important role in the molecular adsorption and sensing mechanisms. In the future, it may be beneficial to study the sensing performance of GNRs of different width and length to understand the mechanisms behind the high sensitivity of GNR NO₂ sensors.

VAPOR-PHASE TRANSPORT DEPOSITION, CHARACTERIZATION, AND APPLICATIONS OF LARGE NANOGRAPHENES:

In this section, we report our finding that films of large nanographene molecules can be prepared using vacuum sublimation without destroying their aromatic core structures. Specifically, we developed a vapor-phase transport (VPT) approach, in which the large nanographene molecules are sublimated on a substrate in a vacuum-sealed glass tube. These films comprise of stacked large nanographene molecules maintaining their aromatic cores, without fusion or fragmentation. FETs based on such films exhibited current on/off ratios in the range of 140 - 170. We chose two kinds of

large nanographene molecules which have been considered to be too large for vacuum sublimation (Figure 4). We used atomic force microscopy (AFM), matrix-assisted laser desorption/ionization timeof-flight mass spectrometry (MALDI-TOF MS), and Raman spectroscopy to characterize the film morphology, to compare the pristine material with the sublimated films, and to ensure that the deposited large nanographenes in the films maintained their basal plane structures. The results showed that the basal plane of large nanographenes can be maintained under the conditions we have used. Moreover, we showed that graphene nanopatch (GNP) and C₉₆ films (Figure 4) can be used in the fabrication of thin-film transistors (TFT) with improved current on/off ratios by sublimating the molecules of choice onto substrates with prefabricated electrodes (Figure 5). Besides the observation of uniform films, we have also observed crystal-like island structures upon sublimation of GNPs, which have shown even higher electrical conductance than the films. The GNP crystal TFT demonstrated a field-effect mobility of $\sim 1 \text{ cm}^2/\text{V.s.}$, which can be further improved by improving the contact resistance and the thickness of the crystal. Our VPT approach to prepare pristine nanographene molecular films suggest great promise for the future implementation of large nanograppenes in electronic, optoelectronic and sensing applications.

SUMMARY:

In summary, we have studied three different types of GNRs in this project. First, we examined the potential for using HIBL to pattern narrow and aligned GNRs. We have successfully patterned 5 nm half-pitch GNRs, which is the smallest pitch reported to date. Then, we studied ultra-long (500 nm) chemically synthesized GNRs. We were able to deposit individual GNRs, and films of such GNRs and characterize their electrical, optical and chemical sensing properties. Finally, we developed a vapor-phase transport technique to create films of chemically synthesized large nanographene molecules. We have successfully fabricated TFTs based on such films and showed the potential of crystalizing such molecules for high performance TFTs.

FIGURES:

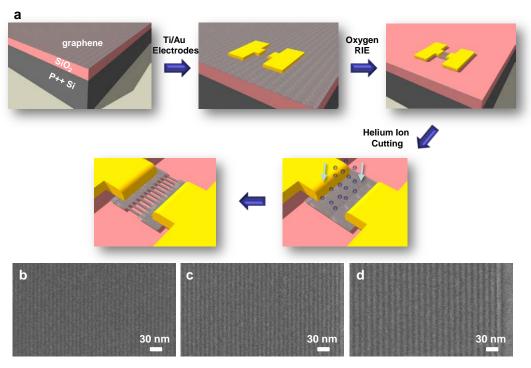


Figure 1. a) Scheme of GNR array devices fabricated by HIBL. b, c, d) Helium ion microscope images of 5nm, 6nm and 7.5 nm half-pitch arrays.

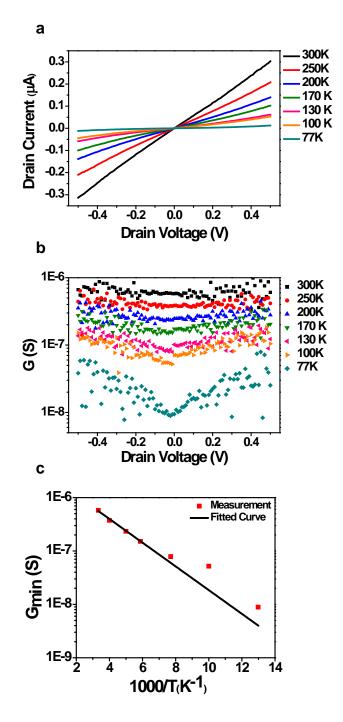


Figure 2.Temperature-dependent electrical measurements of 5nm wide and 200 nm long GNR array: a) Output characteristics of the device under different temperatures. b) Minimum differential conductance (G_{min}) variation *versus* drain voltage at different temperatures. c) Minimum conductance vs. inverse temperature and the corresponding curve fitting. The gate voltage was 0V.

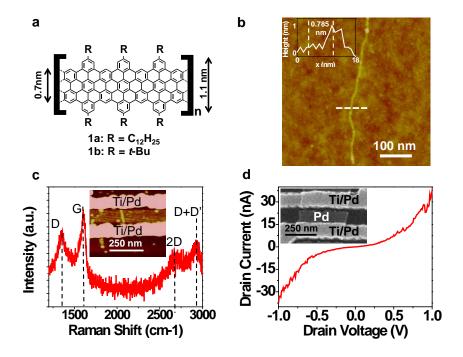


Figure 3. a) Chemical structure of GNRs **1a** and **1b**. b) AFM tapping mode height image revealing synthesized GNR length > 500 nm. Inset showing a height profile of the GNR (at the dashed line) revealing a height of 0.785 nm. c) Raman spectrum of an individual GNR revealing D, G, 2D and D+D' bands. Inset shows an individual GNR between two Ti/Pd electrodes. d) Current vs. drain voltage (I-V_d) characteristic of an individual GNR device after metal angle deposition with a channel length of ~ 20 nm. Inset showing an SEM image of a 20 nm gap between Ti/Pd and angle-deposited Pd.

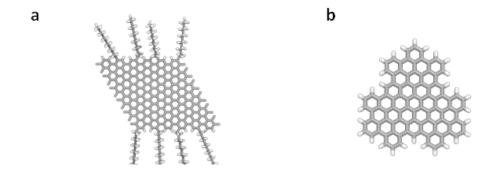


Figure 4. Molecule structure, vapor-phase transport deposition, and characterization of the nanographene molecules . **a**) Molecule structure of graphene nanopatch (GNP) (dangling bonds at edges indicate longitudinal repeat of such structure). **b**) Molecular structure of C_{96} molecules used in this study. Carbon and hydrogen atoms are represented in grey and white respectively

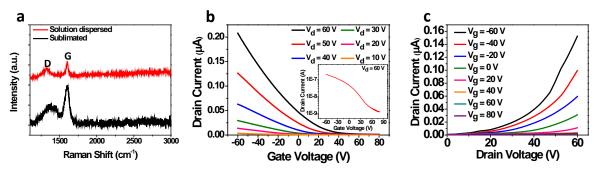


Figure 5. a) Raman spectra of GNP films prepared by liquid-phase processing and sublimation. **b)** I_d - V_g characteristics of a GNP film TFT at different drain biases. Inset shows a logarithmic scale I_d - V_g curve of GNP film TFT showing a current on/off ratio of ~174. **c)** I_d - V_d characteristics of the GNP film TFT at different gate voltages showing highly non-linear curves indicating a Schottky contacted TFT.

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